Report for 2003IA35B: Tracing Sediment Sources in Eastern Iowa by Using Stable Carbon and Nitrogen Isotopes: An Exploratory Research

There are no reported publications resulting from this project.

Report Follows

Tracing Sediment Sources by Using Stable Carbon and Nitrogen Isotopes: An Exploratory Research

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Summary

A fingerprinting technique that can help in elucidating the pathways of soil particles and temporal discontinuities in soil delivery is developed. Our composite fingerprint—due to its simplicity, low sampling requirements, and unique ability to distinguish soils produced from different land uses—can be effectively used in large-scale watersheds to quantify soil movement. The ability of our method to identify soil sources over large scales and to quantify soil movement at short time scales is inherent in the use of C-13, N-15, and C/N fingerprints. The stable isotope C-13 reflects the signature of the parent vegetation at different spatial scales; the mean elemental atomic ratio C/N ratio is reflective of plants and microorganisms that have inhabited the soil at different spatial scales; and the stable isotope N-15 reflects the temporal variations in the organic content of soils, primarily due to volatilization and organic decomposition. Our approach leads to the development of a composite tool that, for the first time, incorporates both statistically verified isotopic signatures of soils and a mixing optimization model to (1) identify the soil provenance originated from contrasting land uses; and (2) provide the proportion of soil particles produced by different land uses.

Introduction

Unwarranted soil erosion creates problems for land users, watershed ecosystems, and riverine habitats. While an urgent need exists to control soil erosion, mitigation is delayed as watershed managers and engineers are often unable to identify and measure erosion sources. Conceptually, soil erosion is easy to visualize. Soil stored in upland slopes erodes through fluvial erosion or mass failure (i.e., landslides, bank failure) to footslopes and floodplains, where it is either stored temporarily or continues movement into streams. While seemingly simple, measuring soil erosion has proven a complicated task; and existing monitoring techniques, such as erosion pins, erosion troughs, and scanning laser altimetry (LIDAR) are often expensive and face important spatial and temporal sampling constraints at the watershed scale. Spatial fractionalization of suspended soil serves as a practical approach to measure erosion from spatial regions within a watershed.

Spatial fractionalization refers to a field-based monitoring procedure that measures the relative soil eroded from spatially defined regions within a watershed. Spatial fractionalization involves a three-step process, including: (1) capturing eroded soil at the watershed outlet, (2) measuring the distributions of bio-chemical, geo-chemical, mineral magnetic, radionuclide, and/or physical soil properties, and (3) using the properties to partition or fraction the eroded soil into components derived from spatial regions within the watershed. The term fractionalization is derived from sediment transport literature. Fractionalization is traditionally used to define the distribution of particle sizes for stream sediments. Similarly, spatial fractionalization of soils defines the distribution of source-soils within the eroded sample.

Spatial fractionalization of eroded soils has been used previously, typically by researchers in the geologic, pedologic, and geographic fields under different taxonomy (e.g., suspended sediment fingerprinting, soil tracing). This past work has widely utilized mineral magnetic, geo-chemical, and radionuclide properties to connect suspended soils with their spatial provenance via a multivariate,

error-minimization model (i.e,. un-mixing model). At the watershed scale (>500 km^2), research has focused primarily upon fractionalizing eroded soils from pedologically contrasting sub-units (i.e., different soil associations) dependent upon geologic diversity.

The work herein aims to establish the use of nitrogen-15, $d^{15}N$, and carbon-13, $d^{13}C$, stable isotopes, and the C/N atomic ratio as bio-chemical soil properties that may be used to spatially fractionalize eroded soil from different source-soil land uses—herein from forest vs. agriculture land uses—at the watershed scale. Spatial fractionalization based on land use is important because forest vs. agriculture soils have very different erosion rates. For example, fields used for crop production are, typically, a significant source of fine soil particles because the soil surface is disturbed through several tillage operations over the growing season. On the other hand, forests are more stable, with lower amounts of soil delivery, unless disturbed by natural disaster or human activity. Quantifying these differences using spatial fractionalization will benefit erosion prediction model development and will aid watershed managers in decision strategies.

It is well documented that soil consists of inorganic and organic constituents within a composite aggregate matrix. The organic constituent is reflective of vegetative cover and land management (e.g., fertilizers, nutrient cycling due to tillage practices), and $d^{15}N, d^{13}C$ and C/N properties may be used to quantify these organics. $d^{15}N, d^{13}C$ and C/N are based on carbon and nitrogen atomic arrangement within soil and are dependent upon a number of processes, such as vegetation decomposition, fertilizer sorption, and denitrification. These processes are altered due to soil-environmental factors, such as vegetation type, soil moisture and temperature, concentration of soil gases, and land/crop management. Therefore, variations in $d^{15}N, d^{13}C$ and C/N exist when comparing forest vs. agriculture land uses but also may exist when moving across the landscape, deeper into the soil profile, to different plot locations within the same land use or during seasonal extreme conditions. Identifying the significant factors that induce variation of $d^{15}N, d^{13}C$ and C/N, and explaining that variation, is the thrust of the research presented herein. If the variation of $d^{15}N, d^{13}C$ and C/N may be accounted, then the soil properties may be adequately used for forest vs. agriculture land use fractionalization.

Recently, Papanicolaou et al. (2003) explored the feasibility of using $d^{15}N, d^{13}C$ and C/N for spatial fractionalization purposes in the Upper Palouse Watershed, Northwestern Idaho. However, $d^{15}N, d^{13}C$ and C/N variability warranted further experimental investigation within forest and agriculture land uses. The objective of the present report is to utilize 231 original soil data from the Upper Palouse Watershed to specifically address $d^{15}N, d^{13}C$ and C/N variation based on spatial and temporal factors including: land use, slope location, plot location within a given land use, sample depth in the soil profile, and sampling season. It is expected that the results presented herein will be utilized to further establish spatial fractionalization of forest vs. agriculture land uses as a soil erosion measurement technique at the watershed scale.

Background Regarding $d^{15}N, d^{13}C$ and C/N

As previously mentioned, $d^{15}N, d^{13}C$ and C/N are soil properties based on carbon and nitrogen atomic arrangement within soil organics. In the following subsections, a brief introduction of the three

bio-chemical properties is presented including a discussion of the processes influencing variation. Realization of $\delta^{15}N, \delta^{13}C$ and C/N spatial and temporal variation sets the framework for the experimental investigation detailed in the methods.

$\underline{\delta^{15}N}$. $\delta^{15}N$ is a signature proportional to the *15N:14N* isotopic ratio and has been used most prominently by environmental scientists to study nitrogen pollution in the hydrosphere and atmosphere; but $\delta^{15}N$ has also been used significantly for studying issues such as nitrogen cycling in plants and nitrogen cycling in lakes and coastal regions. While $\delta^{15}N$ fractionation—defined as the partitioning of isotopes (i.e., 15N and 14N) and thus the altering of $\delta^{15}N$ —within soil environments has been difficult to implicitly quantify and is still under investigation, it is accepted that the variation of $\delta^{15}N$ values for inorganic and organic soil constituents is induced by processes including assimilation, mineralization, volatilization, denitrification, and decomposition. These processes are accompanied by fractionations, whereby plants or soil discriminate between nitrogen isotopes, tending to favor the incorporation of *14N* over *15N* or visa versa, and, thus, the soil $\delta^{15}N$ value is depleted or enriched. $\delta^{15}N$ values are typically higher for agriculture soils as compared to forest soils under similar environments.

$\underline{\delta^{13}C}$. $\delta^{13}C$ is a soil property proportional to the *13C:12C* isotopic ratio which highly retains the signature of the parent vegetation. That is, $\delta^{13}C$ of soil reflects that of vegetation with only a small enrichment during decomposition. Due to this fact, $\delta^{13}C$ has been extensively used in the soil research for paleo-environmental studies of changes in vegetation and climate and to investigate soil carbon dynamics.

The well documented difference in $\delta^{13}C$ values for C3 and C4 plants induced by the unique photosynthetic pathway of each plant type results in the average plant tissue $\delta^{13}C$ values of –12‰ for C4 plants and –26‰ for C3 plants. Within the C3 or C4 plant types, $\delta^{13}C$ values of individual plant species can additionally vary by several parts per mil and are dependent upon a number of factors including soil water, humidity, genetic response to water or salinity stress, drought stress, irradience levels, plant nutrition, altitude, and the assimilation of soil repired CO_2 in closed canopies. Thus, forest vs. agriculture soils attain distinct $\delta^{13}C$ fingerprints due to contrasting vegetation and distinct environmental regimes.

<u>*C/N.*</u> The *C/N* atomic ratio—defined as the ratio of total atomic carbon to total atomic nitrogen—exists as a proxy typically used for ecosystem health and processes by soil fertility experts. The soil *C/N* ratio is reflective of plants and microorganisms which have inhabited the soil. Terrestrial plants have a wide *C/N* ratio range primarily between 10 to 40 (e.g., gymnosperms=16.4; pteridophytes-ferns, plants with spores=25.6); however, values as high as 90 are not uncommon. Most microorganicsms have *C/N* ratios between 4 and 9. As plants decompose, the trend is the loss of carbon due to microbial oxidation and respiration of CO_2 and the sequestering of nitrogen, resulting in a decrease of the soil organic matter *C/N* ratio relative to plants. A number of reasons account for differences in *C/N* when comparing forest vs. agriculture soils, including vegetation type, decomposing organic complexes, carbon and nitrogen losses during cultivation, and chemical fertilizers.

Study Watershed

Figure 1 illustrates the study area located within the Upper Palouse Watershed in Northwestern Idaho. Figure 1 details the designated watershed outlet within the city limits of Princeton, Idaho, located upstream of river mile 140 at Hattercreek Creek Road Bridge 1, approximately ½ mile south of the junction of Idaho SR 6 with Hatter Creek Road. This reach drains an area of approximately 600 km^2. The Palouse River, a gravel bed-cohesive bank river, and its tributaries occupy the drainage of the watershed. The majority of the study area is either public land controlled by the USDA Palouse Conservation Field Station, and is a target watershed designated by the Natural Resources Conservation Service (NRCS) for water quality and soil erosion research, or is part of the St. Joe (Clearwater) National Forest.

The Palouse River watershed was chosen due to its variable land uses. Deep intermountain valleys with relatively small floodplains characterize the upper portion of the Palouse River watershed. This topography prevails above Laird Park, located at elevation 809.4 m above mean sea level (Palouse Subbasin Summary, NWPPC 2001). In these upper portions of the watershed, the land is predominantly conifer forest. This region comprises the forest sampling area, and locations are illustrated in Figure 1. Rolling hills used for agriculture (primarily wheat and hay) dominate downstream of Laird Park. The hills have 15.6 % to 27.9 % steepness at approximately 750 m above mean sea level. About half or less of this cropland is in annual production. Roughly, there is a two- to three-year rotation of winter wheat/spring lentils or peas, or winter wheat/spring barley/spring lentils or peas. The remainder of the cropland is permanent grass used for hay or grazing, or is committed to the Conservation Reserve Program. This lower portion of the watershed comprises the agriculture sampling areas of the study and sites are illustrated in Figure1.

The climate in the Palouse Watershed consists of generally mild winters and summers punctuated by occasional high or low temperatures. The soil of the basin can freeze to 20–30 inches of depth during the more extreme winters. The average annual precipitation (1961–1990) is 536 mm, falling mostly between October and May. The main erosion season is late winter to early spring, at which time approximately 249 mm of the annual precipitation occurs. As much as 90% of the soil loss is caused by surface thaws and snowmelt, primarily during February and March. The watershed soils are formed in a combination of parent materials including loess derived from south central Washington, underlying geologic rock, and volcanic ash from the eruption of Mt. Mazama approximately 8,000 years ago.

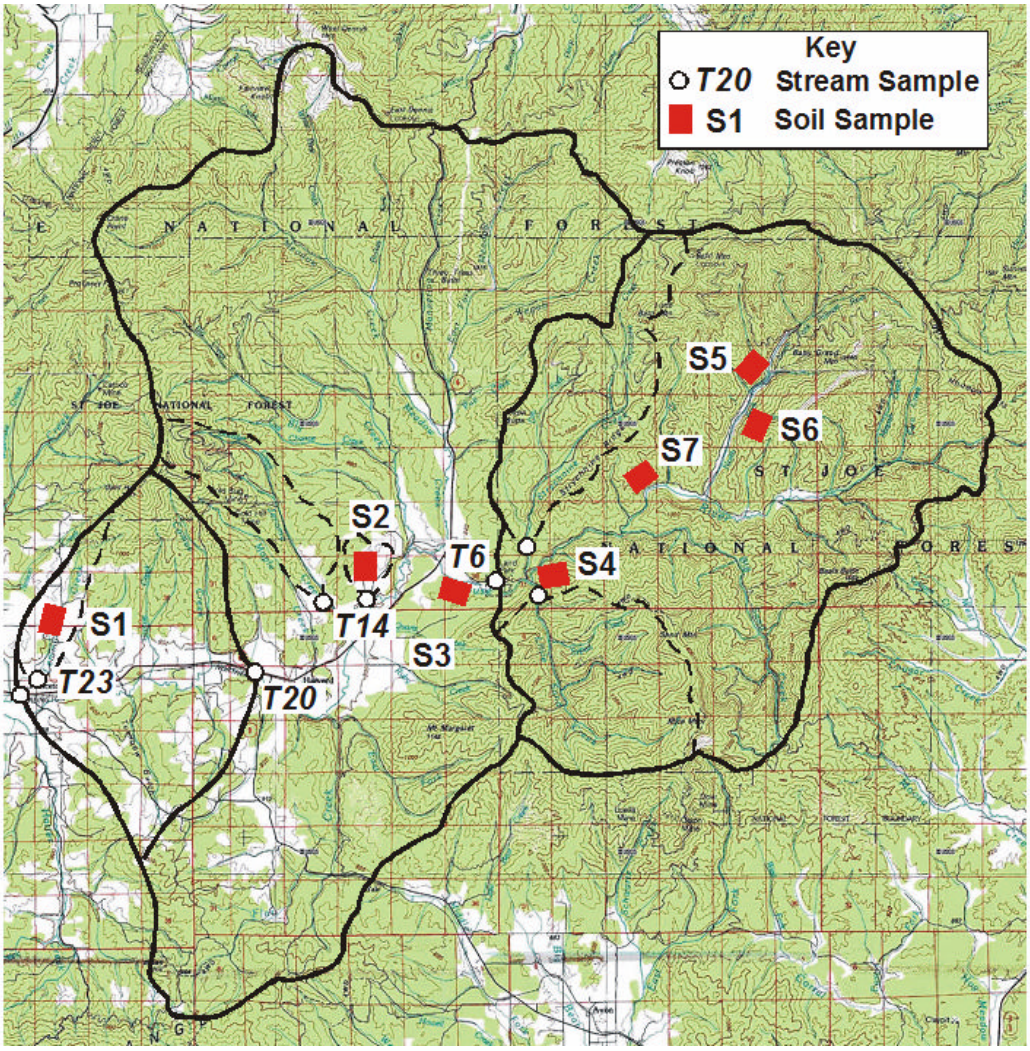


Figure 1. Upper Palouse Watershed and designated sampling sub-watersheds. Stream sampling and soil sampling locations are depicted with white circles and red rectangles, respectively.

Methods

Herein, a sampling experimental design is established and completed with the intent of capturing spatial and temporal variation of $d^{15}N, d^{13}C$ and C/N. The following sub-sections present details regarding soil sampling, lab procedures, and isotopic analyses.

Soil Experimental Design and Field Sampling. The experimental source-soil sampling design is established with the intent to explain $d^{15}N, d^{13}C$ and C/N variation via statistical analysis of variance (ANOVA). $d^{15}N, d^{13}C$ and C/N are established as three independent response variables, and a set of factors are varied during sampling to assess their effect on each response variable. Factors are chosen to represent pedologic variation within the watershed soils; thus a range of soil processes is indirectly accounted. Factors considered most relevant to induce $d^{15}N, d^{13}C$ and C/N alterations include: (1) *land use* (i.e., agriculture vs. forest), (2) *plot location* of sample within the land use, (3) *slope topography* of sampling, (4) *season*, and (5) *profile depth.*

Land use is the focus of this study and is expected to produce $d^{15}N, d^{13}C$ and C/N differences due to vegetative cover and land management. Over 100 samples are excavated within each land-use to provide 200+ samples for source-soil distributions. Plot location induces elevation and, thus, climatic gradients and has been shown to modify carbon isotopic composition of plants. In addition, various plot locations may introduce soil variation due to differing land management and pedologic history; therefore, numerous plots are sampled within both the forest and agriculture land uses. Table 1 compiles the plot location names, and Figure 1 illustrates plot locations with a red box for sampling.

Table 1. Names of soil sampling plot locations.

Number	Name	Description
1	Pienesta Grove	AG - 2650'
2	Private Land	AG - 2750'
4	Flooplain near Laird	AG - 2550'
5	Laird Park	FOR - 2600'
6	Eldorado Gulch	FOR - 3200'
7	N.F. of Palouse R.	FOR - 3000'
8	Student Sample location	FOR - 2700'

Slope topography may create microclimates and affect soil moisture conditions—important for denitrification and decomposition processes. To assess these possible effects on $d^{15}N, d^{13}C$ and C/N values, sampling is completed high on the slopes, referred to here as "slope samples," and at the toe of the slope near waterways, referred to here as "floodplain samples." Typically, sampling includes three repetitions at the slope and floodplain locations to address random variability among plots.

Seasonal sampling is deemed important because extreme experimental drought treatments have modified stable carbon isotope ratios by as much as 2‰ for plant species. This past work introduces uncertainty for soil isotopic values; therefore, sampling is completed in eight seasons to assess seasonal variability. In March 2003, sampling was restricted to one forest location due to inaccessible forest roads.

When excavating deeper into the soil profile, an older, more highly decomposed organic constituent is attained; therefore, sampling of the surface topsoil (0–5 cm) and subsurface soil (5–20 cm) is completed to assess $d^{15}N, d^{13}C$ and C/N variation among profile depth. Soil deeper than 20 cm is not sampled due to the fluvial-erosion mechanism and low probability of very deep soils experiencing erosion.

Sampling techniques for soils rely on accepted methods of pedologic and environmental scientists. For each sample, soil pits are excavated and one sample is removed from the 0–5 cm level, omitting the root mat and litter layers from the agriculture and forest soils, respectively. A second sample is then removed from deeper in the profile, generally 5–20 cm. The samples are individually wrapped in aluminum foil, labeled, and placed into plastic Zip-lock bags. Aluminum foil is chosen due to its

absence of carbon or nitrogen components and, therefore, a decreased chance of contaminating soil during transport and storage. Packaged samples are placed into a cooler in order to keep samples close to field conditions (i.e., cool and free of light) until return to the laboratory.

Lab Methods. In the lab, sub-samples for $d^{15}N, d^{13}C$ and *C/N* analysis are removed from each field soil and placed in an aluminum drying dish, labeled with a lab control number, weighed, and dried at 55°C until a constant weight is reached. Roots and plant material representing coarse particulate organic matter, coarse POM, and detritus (i.e., diameter, $d > 250$ µm) are removed from soils, and the samples are ground. Soil particles with diameter, $d < 250$ µm are targeted due to their fate as eroded soil. Soil particulates with $d < 250$ µm, are termed mineralized-SOM ($d < 52$ µm) and fine-POM (52 µm $< d <$ 250 µm) by environmental scientists. By indicating the $d < 250$ µm size range, a highly recalcitrant (i.e., non-labile) organic matter fraction is targeted and, thus, conservative soil properties are attained. Soil samples are checked for carbonates (i.e., inorganic sedimentary carbon), and all soils passed the effervescence test.

Isotope Analysis. Following preparations, sub-samples are transported to the University of Idaho Natural Resources Stable Isotope Laboratory. For isotopic analysis, the material is packed into tin cups, sealed and flash-combusted in the presence of oxygen and a series of catalysts and chemical scrubbers in the Carlo Erba CHN-2500. CO_2 and N_2 produced during combustion are separated with a GC column and delivered by a continuous flow inlet system to a Finnigan MAT Delta Plus isotope ratio mass spectrometer. The mass spectrometer ran in "jump" mode to direct first the CO_2 and then the N_2 beams to the Faraday cups. Precision of this method is typically better than 0.2‰ for nitrogen and 0.1‰ for carbon. Reference gas peaks are placed immediately before and after the sample peaks to correct for instrument drift. Samples of dried egg albumen calibrated against an NIST standard are placed in every tenth position in the runs to provide a means of correcting the data to a known standard. The mass spectrometer analysis ultimately provides the C/N ratios and the isotope ratios for $^{13}C/^{12}C$ or $^{15}N/^{14}N$.

All *C/N* values reported in this paper are expressed in the form of atomic ratios and are dimensionless numbers. Isotope data for carbon and nitrogen are expressed in "*delta*" (d) notation indicating depletion (-) or enrichment (+) of the heavy (higher-mass) stable isotopes ($^{13}C, ^{15}N$) compared to the lighter-mass stable isotopes ($^{12}C, ^{14}N$) relative to standard materials. Because of the small differences in isotopic ratios, the delta values are commonly multiplied by 1,000 and termed per mil (‰) notation, so that the resulting numbers are greater than 1 or -1, depending on the sign. The *delta* notation (d) refers to differences between the isotopic ratio of the sample and accepted standard materials expressed as:

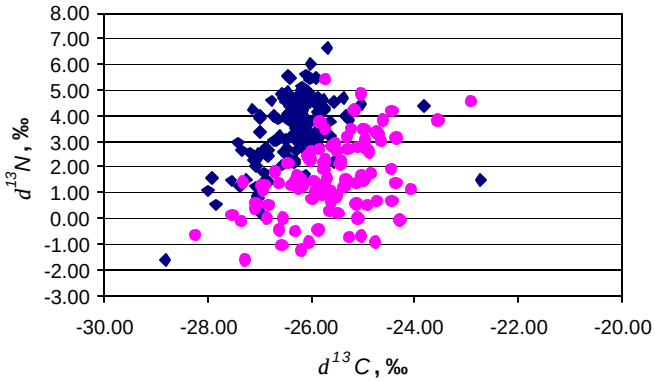
$$dX\ (in\ ‰) = \left(\frac{R_{sample}}{R_{std}} - 1 \right) \bullet 10^3 \qquad (1)$$

where X in our case ($^{13}C, ^{15}N$), R_{sample} is the isotope ratio ($^{13}C/^{12}C$, or $^{15}N/^{14}N$) of the sample and R_{std} is the isotope ratio of the standard (Vienna Pee Dee Belemnite, VPDB, and atmospheric nitrogen, respectively). The dX is measured by mass spectrometry in the laboratory (for more details see the methods/under tasks section).

Results

Figure 2 illustrates scatter plots of a) $d^{15}N$ vs. $d^{13}C$, b) C/N vs. $d^{13}C$, and c) $d^{15}N$ vs. C/N for the 231 soil data. In the figure, pink circles represent forest data and blue diamonds represent agriculture data. Values are presented separately on *x*- and *y*-axis with $d^{15}N$ and $d^{13}C$ in units of ‰ and C/N as dimensionless.

a)



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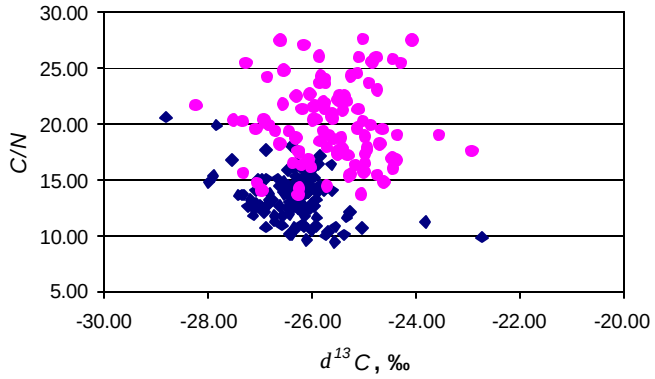

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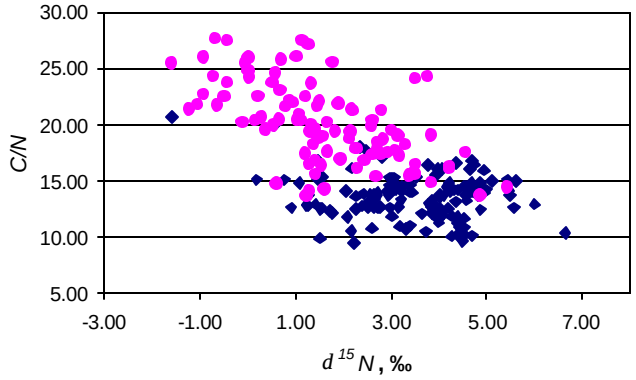

Figure 2. Scatter plots of a) $d^{15}N$ vs. $d^{13}C$, b) C/N vs. $d^{13}C$, and c) $d^{15}N$ vs. C/N for the 231 soil data. In the plots, pink circles represent forest data and blue diamonds represent agriculture data. Fingerprint values are presented separately on *x*- and *y*-axis with $d^{15}N$ and $d^{13}C$ in units of ‰ and C/N as dimensionless.

The plots qualitatively display the separation of the forest and agriculture data using the soil properties. The plots illustrate the variability associated with the soil properties for the spatial and temporal sampling throughout the watershed but offer promise for the soil properties as a spatial fractionalization tool. In the following sub-sections, results of soil $d^{15}N, d^{13}C$ and C/N isotopic analysis are presented, and the statistical analyses to assess variability are established. Soil sample results are evaluated with the ANOVA analysis to address variation of $d^{15}N, d^{13}C$ and C/N, focusing upon variation based on spatial and temporal factors. Within ANOVA, $d^{15}N$ or $d^{13}C$ or C/N are used independently as response variables, and land use, plot location, season, profile depth, and slope location are specified as factors. ANOVA models are performed for each response variable (i.e., $d^{15}N$ or $d^{13}C$ or C/N) with the inclusion and exclusion of factors and factor interactions. Results of the analysis are included herein for only the models which highlight the prominent role of the factors and best explain data variation. Analysis of means (ANOM) is also administered in order to quantify values for the trends deciphered from ANOVA. *Minitab Statistical Software 13.0* is utilized for the ANOVA and ANOM analyses.

$d^{15}N$ **Variation.** Table 2 illustrates the results of ANOVA "Model 1" with $d^{15}N$ as the response variable and land use, profile depth, slope location, the interaction of land use and slope location, plot location, and season as factors. In Model 1, plot location is specified as nested within land use (i.e., PlotLoc(Land-use)), that is, plot locations 1–4 in Table 2 are only associated with agriculture land use, and plot locations 5–8 are only associated with forested land use. Table 2 compiles F and p-values indicating the factor's importance and the probability for the factor's effect to be insignificant; therefore, a low p-value indicates high significance. In Model 1, land use, profile depth, and plot location exhibit significance as factors, indicated by their low p-values, < 0.0001.

Table 2. Results of ANOVA Model 1 for $d^{15}N$ variation.

Factor	F	P
Land Use	43.370	0.000
Profile Depth	20.410	0.000
Plot_Loc(LandUse)	17.550	0.000
Slope Location	1.820	0.165
LandUse*SlopeLocation	2.010	0.137
Season	3.240	0.023

Table 3 presents the ANOM for the land use factor and includes all 231 soil data. $d^{15}N$ values are 3.46 and 1.59‰ for agriculture and forest land uses, respectively. The values differ as compared to preliminary data for the Palouse Watershed (i.e., forest mean $d^{15}N$ = 0.78‰ vs. agriculture mean $d^{15}N$ = 4.74‰), primarily attributed to the inclusion of multiple plot locations in the new data (Papanicolaou et al., 2003); however, the trend of an increase in $d^{15}N$ value of agriculture soil relative to forest soil is maintained in the more extensive dataset. This trend agrees well with forest vs. agriculture $d^{15}N$ values in other physiogeographic regions.

Table 3. ANOM for agriculture and forest land use soils.

Land Use	Samples	$d^{15}N_{AIR}$	$d^{15}N_{AIR}$	$d^{13}C_{PDB}$	$d^{13}C_{PDB}$	C/N	C/N
		Mean	StDev	Mean	StDev	Mean	StDev
		‰	‰	‰	‰	-	-
Agriculture	134	3.46	1.33	-26.35	0.68	13.48	1.97
Forest	97	1.59	1.47	-25.65	0.90	20.07	3.56

Conclusions

Our findings from the research can be summarized as follows:

1) $d^{13}C$ reflects the signature of the parent vegetation effectively and can clearly distinguish soils produced by land uses with contrasting parent vegetation (C3 vs. C4).
2) $d^{13}C$ can distinguish soils produced from different plot locations, even in monoculture environments, if the factors related to C biogeochemical cycle introduce variations that are greater than the variation (error) introduced by the isotopic analysis performed via the mass spectrometer. Mass spectrometer errors do not typically exceed 0.1 ‰ .
3) C/N is an effective indicator of different land uses.
4) $d^{15}N$ has the highest variation in comparison to the other two fingerprints (see figure 1(b)).
5) The factors considered most relevant to induce $d^{15}N, d^{13}C$ and C/N alterations include: (a) land use, (b) plot location of sample within the land use, (c) slope topography of sampling, (d) season, and (e) profile depth. These factors depict pedologic variation within the watershed soils; thus, a range of biogeochemical soil processes is indirectly accounted.
6) Well established statistical tools can be used to adequately describe the factors considered most relevant to induce $d^{15}N, d^{13}C$ and C/N alterations.

Based on the Palouse Watershed study, it was concluded that some research issues must be further investigated, including:

1) The fact that $d^{15}N$ presents a high variability can be advantageous for conducting short-term erosion studies as long as the prominent factors introducing such variability are understood and their variability can be statistically verifiable.
2) In order to develop a reliable composite tool, the spatial variability of the signatures as function of the above factors needs to be considered and modeled via statistical tools.
3) The Palouse study is limited to the fingerprinting of agriculture and forest land uses. The contributions of roads, gullies, and other sources need to be explored in the future research if the development of a general fingerprint tool is the ultimate goal.
4) Soil samples used for isotopic analysis and soil fingerprinting should offer adequate spatial and temporal representation of the different signatures.

References

Papanicolaou, A., Fox, J., and Marshall, J. (2003). Sediment Sources Fingerprinting in the Palouse River Watershed, USA. *International Journal of Sediment Research*. 120:23–29.